

Experiments also were carried out to detect the presence of isocitratase in the rat liver preparation. The assay procedure adopted was that of Kornberg and Beevers.⁴ Up till now it has not been possible to detect this enzyme activity by the assay procedure adopted, perhaps because the supernatant preparation which had both isocitric dehydrogenase and glyoxylic acid reductase activities may have caused the removal of both isocitrate and glyoxylate. A similar situation also was faced by others¹¹ while working with castor bean preparations. Further work in this line is in progress with some modified system for the test of isocitratase activity, and a full account will be published elsewhere.

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(11) A. Marcus and J. Velasco, *J. Biol. Chem.*, **235**, 563 (1960).

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THE OSMOTIC APPROACH TO THE PHENOMENON OF ELECTROLYTE INVASION OF ION-EXCHANGE RESINS

Sir:

The water activity of ion-exchange resins which have been invaded by non-exchange electrolyte has been measured by an isopiestic technique. Preliminary results have been obtained for the systems LiCl-LiR and NaCl-NaR where the symbol R represents Dowex-50 X-S. The resin samples were first equilibrated with external salt solutions of various concentrations to obtain a range of mole fractions of electrolyte within the resin phase. The invaded resin samples after separation from the aqueous salt solutions by centrifugation through a sintered glass disc were placed in test-tubes and allowed to equilibrate with saturated salt solutions which ranged in water activity from 0.9248 to 0.0703, so as to obtain different water contents and thus different molalities at the same electrolyte mole fraction. This method does not appear to have been used previously. The time needed to reach equilibrium varies from a few days to 3-4 months. No effort was made to hasten the approach to equilibrium either by use of silver crucibles and copper blocks to enhance thermal conductivity, by evacuation of the system or by circulation of the water vapor. The ambient temperature of $24 \pm 2^\circ$ was employed.

Thus, one obtains the osmotic coefficient, ϕ , as a function of the total molality for several different mole fractions of salt.

$\log a_w = -0.00782\phi(2m_{MCl} + m_{MR}) + \pi V_{H_2O}/2.303RT$
where a_w = external water activity, m = internal molality, π = swelling pressure, V_{H_2O} = partial

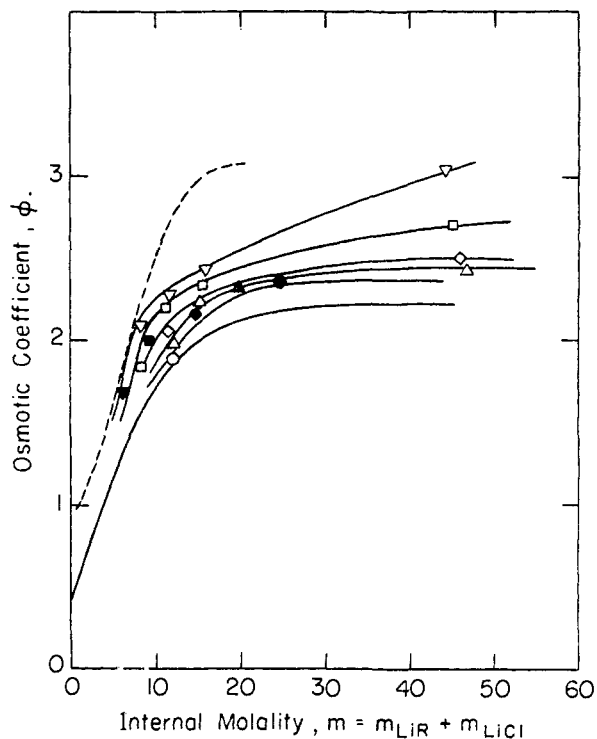


Fig. 1.—Osmotic coefficient as a function of the internal molality, $m = m_{LiR} + m_{LiCl}$: pure LiR —, pure LiCl ---, mole fraction LiCl 0.351 O; 0.303 Δ ; 0.282 \diamond ; 0.217 \square ; 0.100 ∇ . Shaded symbols refer to separated resin samples without additional isopiestic equilibration.

swelling volume of water in the resin phase. The swelling pressure, π , is calculated from the empirical equation of Glueckauf,¹ $\pi = 1.23(V_e - 192)$, for an 8% DVB resin where V_e is the equivalent volume of the swollen invaded resin which is obtained by a direct pycnometric density measurement and the numerical constants represent the modulus of elasticity and the unswollen or matrix resin volume, respectively.

The results for the system LiCl-LiR are presented in Fig. 1 as a plot of the osmotic coefficient, ϕ , vs. the internal molality, $m = m_{LiCl} + m_{LiR}$. The solid points represent values obtained from the separated resin samples without additional isopiestic equilibration. Also included for comparison are the curves for pure 1/2% D.V.B. LiR obtained by Soldano² and by Glueckauf¹ for molalities above 15, and for pure LiCl. The variation of ϕ with composition is not as expected; the curve for a LiCl mole fraction of 0.100 lies closer to that for pure LiCl than does the curve for a LiCl mole fraction of 0.351. The curves for the mixed electrolyte systems could be fitted to an equation of the type used by Soldano for pure LiR

$$\phi = \frac{am}{1 + bm} + \phi_0$$

where a , b and ϕ_0 are constants, since the curves have somewhat similar shapes. If a , b , and ϕ_0 are smoothly varying functions of the composition, these results together with the LiCl activity of the

(1) E. Glueckauf, *Proc. Roy. Soc. (London)*, **A214**, 207 (1952).

(2) B. Soldano and Q. V. Larson, *J. Am. Chem. Soc.*, **77**, 1331 (1955).

initial equilibrating solution permit the calculation of the LiCl activity in any of these mixtures. Data of this type for other cations permit the calculation of exchange selectivities in concentrated solutions. Work is now being extended to more accurate determinations of the osmotic coefficients of mixed resin-electrolyte systems and to measurement of selectivity as a function of mole fraction exchanged in the lower molality region (1-6 molal for NaCl and LiCl systems) where aqueous phase activity coefficients are accurately known.

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REARRANGEMENT OF 1-METHYL- AND
1-ETHYLPENTABORANE-9 TO 2-METHYL- AND
2-ETHYLPENTABORANE-9

Sir:

An apparently quantitative conversion of a 1-alkylpentaborane-9 (R = methyl, I; R = ethyl, II) to a 2-alkylpentaborane-9 (R = methyl, III; R = ethyl, IV) in the presence of 2,6-dimethylpyridine (Fig. 1) suggests a general reaction to obtain 2-substituted pentaboranes.

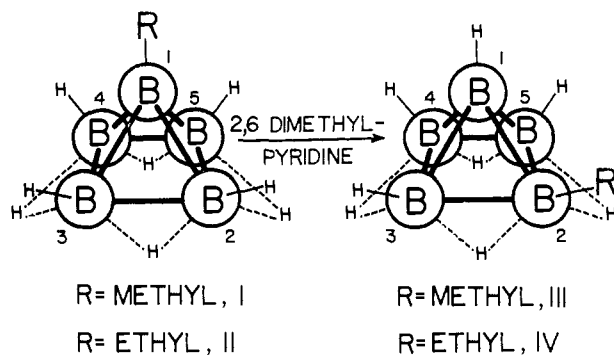


Fig. 1.

A mixture of 0.50 millimole of II¹ and 0.3 ml. of 2,6-dimethylpyridine sealed in a 5-mm. tube exhibited approximately the same B¹¹ nuclear magnetic resonance spectrum as pure II^{1b,2} (doublet $\delta = +13$, $J = 155$ c./s.; singlet $\delta = +39^3$ with area ratios 4:1, respectively). After a period of four hours at room temperature the rearrangement was essentially complete and the B¹¹ n.m.r. profile was that of IV (singlet $\delta = -2$; doublet $\delta = +16$, $J = 160$ c./s.; doublet $\delta = +52$, $J = 170$ c./s.; with area ratios of 1:3:1 respectively). B¹¹ n.m.r. spectra taken periodically during the course of the rearrangement indicated a gradual change from II to IV with no detectable buildup of intermediate substances. The $\delta = +16$ doublet of IV was not quite as sharp as the corresponding

(1) (a) R. E. Williams, U. S. Patent 2,917,547, Dec. 15, 1959; (b) B. N. Figgis and R. L. Williams, *Spectrochimica Acta*, **331**, No. 5 (1959); (c) N. J. Blay, J. Williams, and R. L. Williams, *J. Chem. Soc.*, 424, 430 (1960).

(2) J. N. Shooley, unpublished work.

(3) T. P. Onak, H. Landesman, R. E. Williams and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

doublet of II. This probably is because of the slight environmental non-equivalence of the two types of basal borons with terminal hydrogens in IV (4 and 3,5 positions). Pure IV (0.48 millimole) was isolated after addition of excess boron trifluoride ethyl etherate to the reaction mixture and a subsequent separation of the volatiles by vapor phase chromatography.

Similarly, a mixture of I^{1b} was rearranged to III. The structure of III was confirmed by infrared spectrophotometric and vapor pressure data.⁴

A comparison of the B¹¹ n.m.r. chemical shifts of II, IV and pentaborane^{3,5} reveals a shift of about 13 δ units to lower field when the apex boron of the pentaborane framework is alkyl substituted, and a similar shift of about 14 δ units when a basal boron is alkyl substituted. These "alkyl shifts" are in qualitative agreement with other studies.⁶

The mechanism of the reaction may involve slow "symmetrical" cleavage⁷ of I or II and fast recombination to give III and IV, respectively. Among other possible mechanisms Williams^{6,8} has suggested a plausible internal rearrangement facilitated by hydrogen tautomerism. An extension of the present study into the mechanism of the rearrangement and to other related reactions will be reported subsequently.

The author is indebted to Dr. R. E. Williams for use of Varian nuclear magnetic resonance equipment.

(4) J. H. Lamneck and S. Kaye, National Advisory Committee for Aeronautics, research memorandum E58E12, Sept. 1958.

(5) W. D. Phillips, H. C. Miller and E. L. Muettterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

(6) R. E. Williams, private communication.

(7) R. W. Parry and J. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3554 (1959).

(8) R. E. Williams, "Tautomerism and Exchange in the Boron Hydrides; B¹¹ and H¹ NMR Spectra," *J. Inorg. and Nuclear Chem.*, accepted.

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MECHANISM OF FREE RADICAL DECAY IN
IRRADIATED POLYETHYLENE. EVIDENCE FROM
DEUTERIUM-HYDROGEN EXCHANGE

Sir:

In 1954¹ we postulated that free radicals produced in polyethylene by ionizing radiations decayed by reaction following a random walk migration of the free radical centers through the solid polyethylene. We visualized the jumping of hydrogen atoms along or across molecular chains from a saturated CH₂-group to a free radical center —CH—. This picture of free radical migration has been adopted by Voevodskii, *et al.*² Evidence for the migration of free radicals also comes from the e.s.r. studies of Charlesby and Ormerod.³

In this note we wish to present a new mechanism for the migration of free radicals in solid poly-

(1) M. Dole, C. D. Keeling and D. G. Rose, *J. Am. Chem. Soc.*, **76**, 4304 (1954).

(2) A. T. Koritskii, Yu. N. Molin, V. N. Shamshev, N. Ya. Bulen and V. V. Voevodskii, *Acad. Nauk, S.S.S.R. High Molecular Compounds*, **1**, 1182 (1959).

(3) A. Charlesby and A. Ormerod, paper presented at a conference on "Physics of Polymers," British Physical Society, Bristol, England, Jan. 12, 1961.